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File: USPT

Feb 15, 1977

DOCUMENT-IDENTIFIER: US 4008136 A

TITLE: Process for the treatment of waste water by heterogeneous photosensitized oxidation**Abstract Text (1):**

A composition and method for the oxidation of organic contaminants in waste water by subjection to heterogeneous photosensitized oxidation is disclosed.

Brief Summary Text (1):

This invention relates to the treatment of waste water with an oxidation process thereby rendering the waste water more suitable for disposal or subsequent treatment. In particular, this invention relates to the treatment of waste water by subjecting it to the excited singlet state of oxygen generated by heterogeneous photosensitization and to a composition useful therein.

Brief Summary Text (3):

Waste water treatment is usually divided into three stages: primary, the removal of settleable solids; secondary, the removal of readily bio-degradable contaminates; and tertiary treatment. Tertiary treatment is, generally, the further treatment of waste water after prior treatment has reduced the chemical oxygen demand (COD) to less than about 60 mg/l and the biochemical oxygen demand (BOD) to less than about 20 mg/l. It may also include the removal of disease causing agents, plant nutrients, synthetic organic chemicals, inorganic chemicals, heat, sediments and radioactive substances. Tertiary treatment processes include lime (or other chemical) clarification, filtration, activated carbon adsorption, and ozone treatment.

Brief Summary Text (5):

Other known processes for treating waste water effluents include subjecting the effluent to penetrative ionizing radiation in the presence of oxygen (U.S. Pat. No. 3,533,089), oligodynamic metal salts (U.S. Pat. Nos. 2,927,052 and 2,922,737), ozone and/or ultraviolet rays (U.S. Pat. Nos. 2,070,307 and 1,145,140) oxidation of carbonaceous and nitrogenous matter by biologically active slimes (U.S. Pat. No. 3,817,857), aerobic treatment (U.S. Pat. No. 3,817,858) and treatment with ion exchange resins containing tri-iodide ion (U.S. Pat. No. 3,817,860). None of the disclosed methods are photo-oxidative.

Brief Summary Text (6):

It is the object of this invention to provide a waste water treatment process that has advantages and an environmental impact similar to that of ozone but is significantly less expensive. This new method is described as heterogeneous photosensitized oxidation. The photooxygenation process used in this invention is similar to that called "photodynamic action." The term photodynamic action has long been used to describe phenomena in which biological systems are effectively damaged or inactivated by light in the presence of added "dyes" (compounds having electromagnetic radiation absorption maxima between 320 and 800nm) and molecular oxygen. Oxygen is consumed in the process but the dye is not.

Brief Summary Text (10) :

With some biological heterocycles, singlet oxygen affords almost complete degradation of the molecule. For example, Sussenbach and Berends [J. S. Sussenbach and W. Berends, Biochem. Biophys. Acta., 95, 184 (1965)] have shown that guanine is degraded to carbon dioxide, urea, parabanic acid and guanidine. Thymine is degraded to urea, pyruvic acid, acetic acid and formic acid by treatment with singlet oxygen [R. S. Vickers "The Photooxygenation of Uracil Derivatives -- Mechanistic and Biological Implications" Dissertation, Univ. of Calif., Los Angeles, 1971].

Brief Summary Text (13) :

This aim has been achieved by using a polymer in the form of an ion exchange resin as an inert support for the photosensitizing dye. Most photosensitizing dyes are charged species and by using the appropriate ion exchange resin it is possible to attach the dyes to an ion exchange resin. For example, we have attached cationic dyes such as methylene blue to a cation exchange resin, and we have also attached anionic dyes such as rose bengal to an anion exchange resin. Using these photosensitizing dyes attached to ion exchange resins as photosensitizing resins, it is possible to oxidize organic material to yield the same products as obtained when the dyes were not attached. Since the same products and also the same product ratios were observed when photooxidation was carried out using dyes attached to resins, it may be assumed that singlet oxygen is also involved here.

Brief Summary Text (16) :

Photodynamic dyes have also been shown to cause inactivation of viruses, for example, herpes simplex I and II [T. D. Felber, C. Wallis, E. B. Smith, J. L. Melnick and J. M. Knox, J. Amer. Med. Assoc., 223, 289-292 (1973)]. The heterogeneous photosensitized oxidative process described hereinabove may also be effective to inactivate viruses when present in waste water.

CLAIMS:

1. A process for treating aqueous waste effluents containing organic materials which comprises adding to said aqueous effluents in the presence of oxygen, a water insoluble polymer-based photosensitizer and then photolyzing the resulting suspension with light having wavelengths between 320 nm. and about 800 nm.
3. A process as claimed in claim 1 in which the polymer-based photosensitizer is an ion exchange resin containing a photosensitizing dye.
4. A process as claimed in claim 3 in which the polymer-based photosensitizer is an anionic exchange resin containing rose bengal.
5. A process as claimed in claim 3 in which the polymer-based photosensitizer is a cation exchange resin containing methylene blue.
7. A process, as recited in claim 1, in which a heterogeneous mixture is formed of said aqueous waste effluent and said water insoluble polymer-based photo-sensitizer, said process further including the step of separating said treated waste effluent and said water insoluble polymer-based photosensitizer following said photolyzing treatment.
8. A process for generating singlet oxygen which comprises photolyzing a water insoluble polymer-based photosensitizer with visible light in the presence of oxygen.
9. A process as claimed in claim 8 in which the polymer-based photosensitizer is an ion exchange resin containing a photosensitizing dye.

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L3: Entry 11 of 18

File: USPT

Mar 17, 1992

DOCUMENT-IDENTIFIER: US 5097089 A

** See image for Certificate of Correction **

TITLE: Synthesis of glycerol from formaldehyde

Brief Summary Text (25):

Where an amine is used as the proton abstractor, ease of separation can be enhanced by suitable selection of the hydrocarbon groups of amine. Specific examples of the amines includes triethyl amine, imidazole, pyridine, pyrimidine, piperazine or the strong amidine or guanidine type bases e.g. 1,5,7-triazabicyclo-[4.4.0]dec-5-ene (TBD).

Brief Summary Text (34):

The self condensation product containing dihydroxy acetone as such, as a dimer thereof or as a mixture of the two can be separated from the catalyst components by conventional means e.g. by one or more of the following: precipitation, dialysis, liquid-liquid extraction, ion exchange, membrane separations such as hyperfiltration, vacuum distillation, e.g. steam stripping, and the use of adsorbent materials.

Brief Summary Text (38):

Adsorbent materials may also be used to remove the catalyst system from the reactant product either alone or in combination with any one of the above methods. Typical adsorbents include activated carbons, alumina, silica, metal oxides, supported metals on carbon or metal oxide and ion exchange resins. With certain adsorbent materials, it can be advantageous to regenerate the adsorbent, for example by heating the adsorbent in a suitable atmosphere such as hydrogen, steam or air. Adsorbent treatments are particularly suitable for use in combination with a treatment such as liquid-liquid extraction.

Detailed Description Text (42):

Examples 17-19 demonstrate the use of liquid-liquid extraction, ion exchange resin and carbon adsorbents to separate the self-condensation catalyst from dihydroxyacetone (DHA).

Detailed Description Text (49):

The bromide component from the product of Example 17 was removed using the following procedure. The aqueous layer from Example 17 was pumped through a vertical column (10 mm internal diameter, LHSV=4) containing 10 mls of either an anionic ion exchange resin (for example, Bayer E1338/88) or a carbon adsorbent (for example, Sutcliff-Speakman Carbon 607). Bromide ions were detected by precipitation on addition of silver nitrate solution (0.1M). Precipitation occurred before but not after the ion exchange/adsorbent treatment.

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L4: Entry 4 of 17

File: USPT

May 24, 2005

DOCUMENT-IDENTIFIER: US 6896808 B1

TITLE: Recovery of metal values from aqueous solutions and slurries

Brief Summary Text (25):

It is preferable that if any free cyanide exists in the cyanide aqueous stream, for example copper cyanide aqueous stream, that it is removed by membrane separation prior to the introduction of the water soluble polymeric agent, for example as referred to hereafter the PEI-based polymer. This removal step will have the added advantage of reducing the volume of solution to be treated for copper cyanide removal. The permeate will then contain the free cyanide ions (and be immediately available for recycle) and the retentate will contain the copper cyanide ions in a reduced volume of water. A suitable membrane would be of the types described in, for example, U.S. Pat. No. 4,741,831, U.S. Pat. No. 4,770,784, U.S. Pat. No. 4,895,659, U.S. Pat. No. 5,266,203 and U.S. Pat. No. 5,643,456. The PEI-based polymer may then be introduced into the copper cyanide retentate solution and thus become the feed for the second membrane cartridge. Therefore, this second membrane cartridge may be considered as a "displacement reactor" in which the PEI polymer complexes with the copper and the cyanide ions are displaced. The cyanide ions then report in the permeate and the complexed copper reports in the retentate. Ultrafiltration or nanofiltration may be used to separate the metal imine complex from the cyanide ions as they are displaced from the metal cyanide complex. The metal ion is then released from the polymer by acidification as described in U.S. Pat. No. 5,643,456, or preferably by direct electrowinning in a suitably designed electrochemical cell as will be discussed herein.

Detailed Description Text (39):

The application of the water soluble PEI-based polymer may similarly be used to precipitate iron and capture copper, cobalt, nickel and other water soluble metal ions which are capable of coordinating with the PEI polymer. The valuable metals may then be recovered preferably by direct electrolysis of the metal ion-containing polymer. If necessary, the metal-PEI complex may be concentrated by ultrafiltration or nanofiltration methods.

Detailed Description Text (52):

If either copper cyanide or residual cyanide (precomplexed with zinc or preferably copper) is preferred to be recovered by ion exchange technology, then polymers based upon tertiary and/or quaternary amines, guanidines, or according to Examples 5 and 6, etc may be employed to recover the copper cyanide. A preferred form of these ion exchange polymers is as disclosed in PCT/AU98/00811. These ion exchange polymers are then stripped of the copper cyanide using a high pH solution at temperatures of up to about 60.degree. C. and containing additional stripping aids which include the PEI-based polymers described herein and which may also include sodium benzoate, polyacrylic acids, thiocyanates, etc. The resultant strip solution is then passed through an ultrafiltration unit to separate the free cyanide of return to the leach circuit. If desired, one or more, membrane units of different configuration may be employed to separate the balance of the stripping reagents from the cyanide. Preferably, the copper may be directly recovered from the PEI-containing stripping solution by electrowinning processes. Alternatively, the PEI-based polymer may be acidified to release the copper ions. These copper ions are then recovered as copper metal in electrowinning cells. If desired, additional

copper ions may be included in the acidified solution so that the current efficiency of the electrowinning cells is maintained. Such methods are well known to workers in the copper recovery and refining industries.

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